EUROPEAN SYNCHROTRON RADIATION FACILITY
ESRF User Office
BP 220, F-38043 GRENOBLE CEDEX, France
Delivery address: 6 rue Jules Horowitz, 38043 GRENOBLE, France
Tel: +33 (0)4 7688 2552; fax: +33 (0)4 7688 2020; email: useroff@esrf.fr; web: http://www.esrf.fr

Experimental report on Proposals ID : HE-3832 (FAME-BM30B)

X ray absorption spectroscopy investigation: local order and finite size effect on mass selected iron based nanoalloys

Scientific Background

Bimetallic magnetic nanoparticles are excellent candidates for their potential as high density magnetic storage media that require a Magnetic Anisotropy Energy (MAE) increase necessary at room temperature. At PLYRA[1], magnetic nanoparticles are pre-formed in gas phase using a mass-selected low energy cluster beam deposition (MS-LECBD) technique. The produced clusters are embedded in a matrix, co-deposited with the clusters, to avoid interactions and coalescence and to protect them for transfer into air. The stoichiometry of the clusters can be tuned from the composition of the target rod. Recently, we have studied size effects on the local structure and magnetism of CoPt of 2-4 nm diameter clusters embedded in a carbon matrix upon annealing in vacuum. We have observed a c/a ratio greater than 1 at the Co-K edge and inversely a c/a lower than 1 ratio at the Pt-L3 edge for the L10 phase[2]. In this present proposal, the local ordering upon annealing (in vacuum at 500ºK) has been studied from x-ray absorption spectroscopy measurements (XANES and EXAFS) performed on size selected (2nm) and non-size selected Iron base nanoalloys (FeAu, FePt, FeCo and FeRh) embedded in a matrix (Carbon or MgO).

Sample preparation and Characterization

The possibility to control size, composition and host element offers a wide possibility of fundamental studies in these nanoparticle assembled films. We have measured Fe based bimetallic nanoparticles embedded in matrices with a weak influence on the interface magnetic anisotropy (Carbon) in order to preserve and investigate the intrinsic cluster surface properties. Using MS-LECBD coupled to an electrostatic quadrupole deflector, we have been able to synthesize mass selected bimetallic nanoparticles embedded in an amorphous carbon. The samples are prepared from nanoparticles pre-formed in the gas phase and then co-deposited in UHV with the matrix. Diluted (~ 1% of nanoparticles in volume) nanoparticles assembled films, with quite negligible magnetic interaction among nanoparticles, are obtained by adjusting independently the deposition rate of the nanoparticle and matrix beams. The relative size dispersion, which is around 40% without mass selection, has been lowered to about 7% with the mass selection**.**

As-prepared and annealed nanoparticles were previously characterized using (HRTEM). For size selected and non-size selected samples, the nanoparticles are generally crystallized in a chemically disordered phase. In particular, post-annealing our FeRh cluster assemblies generate the CsCl-B2 ordered phases: well defined [110] superlattice spots indicative of alternating Fe and Rh planes have been obtained from HRTEM experiments. At ambient conditions, bulk B2 FeRh is an anti-ferromagnetic material; but in our annealed B2 FeRh nanoparticles, the magnetic signature has been recently found to be ferromagnetic at low temperature by SQUID and XMCD measurements at SLS.

Experimental results

On our allocated beamtime we were able to systematically pass all our samples annealed and as-prepared, size selected and non-size selected. The beamtime was well organised. The first batch of samples was passed on the first half of the experiment on both the 5d edge of Au and Pt; the second batch was passed on the second half of experiment on both the 3d edge of Fe and Co. Our samples had an equivalent thickness of 1.5 nm of clusters. Each sample was measured for 5 hours on reflectivity at an angle around

[1] PLYRA: http://www-lpmcn.univ-lyon1.fr/plyra/
[2] **"Evidence of $L1_0$ chemical order in CoPt nanoclusters : direct observation and magnetic signature"** F. Tournus, A. Tamion, N. Blanc, A. Hannour, L. Bardotti, B. Prével, P. Ohresser, E. Bonet, T. Epicier, and V. Dupuis, Phys. Rev. B, 77, 144411 (2008)

78°. At the L3-edge of Au edge we passed 8 samples (2 days), 6 FeAu samples compared to 2 CoAu samples in carbon and MgO. We then passed on to the L3-edge of Pt edge where we measured 4 samples (1 day) of FePt. The same 4 samples were passed at the Fe edge (1 day) before stopping for the maintenance day. Then 9 samples were passed at the K-edge of Fe edge (2 days) of different Fe-based bimetallic systems; 3 FeRh samples, 4 FeAu samples as well as 2 FeCo samples. For the last day, we passed on to the K-edge of Co edge where we passed 2 FeCo and 2 CoAu samples (1 day).

The idea was to study separately the finite cluster size effects (size selection to non-size selection), the matrix nature (Carbon or MgO), as well as thermal treatment (annealing compared to as-prepared). A detailed study was performed on the most advanced FeRh system. We obtained well defined curves and we were successful in obtaining a best fit for our EXAFS signal (Figure 1). The fit was performed on two non-size selected FeRh samples one as-prepared and one annealed for 2 hours at 500°C.

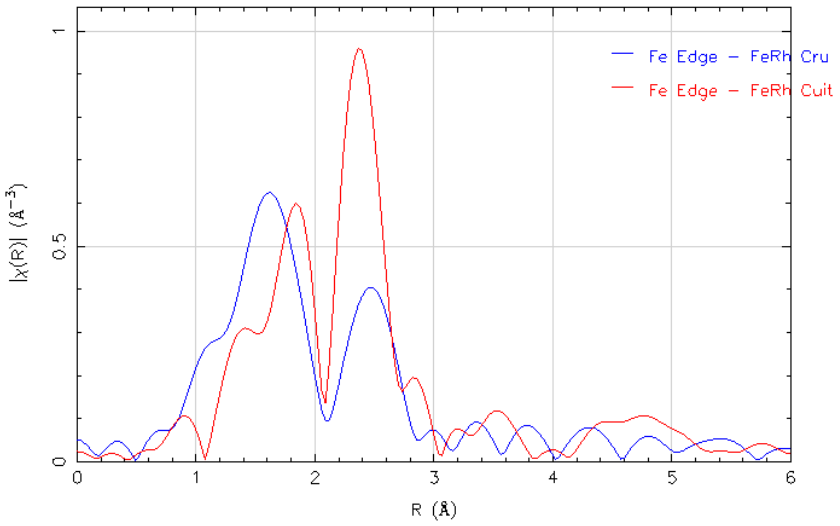

Figure 1 – Experimental Fourier Transform of FeRh clusters annealed and as-prepared

We are in the process of fitting the rest of the data we obtained. We plan on completing the study on our systems one by one starting with the FeRh system. A paper on the FeRh including the EXAFS results has already been accepted in PRL in January 2013.

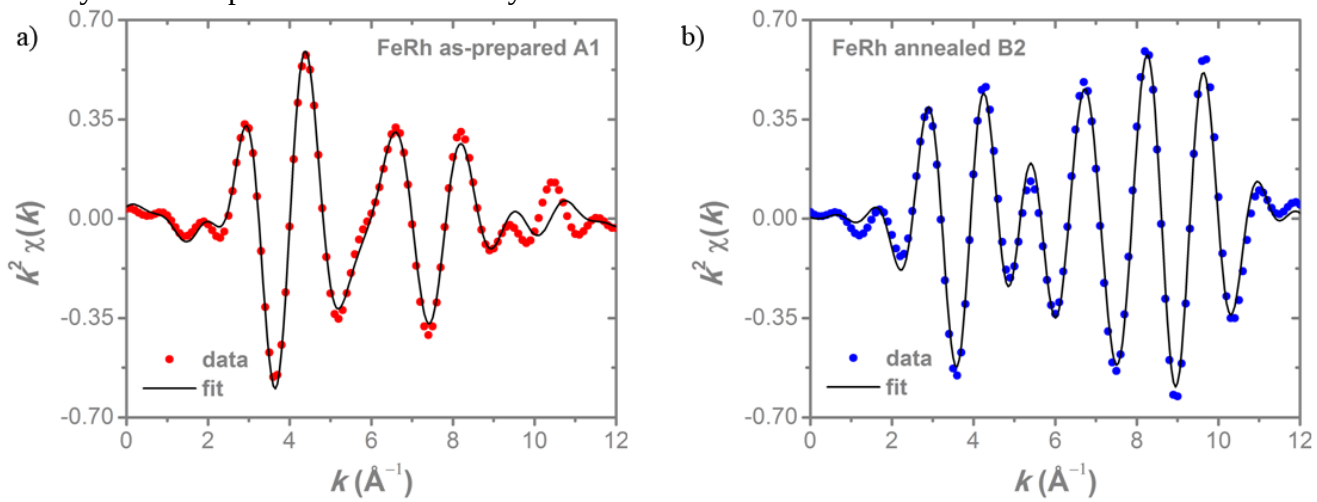

Figure 2- a) and b) Fe K-edge EXAFS data (dots) for the FCC-A1 and CsCl-B2 samples together with fits (lines).

In addition to the EXAFS data, we have scheduled a series of different experiments on our systems including XMCD for magnetic characterization as well as SQUID to complement our structural findings.